SUNWAY UNIVERSITY

Supramolecular Associations Peculiar to Coordination Complexes

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Faculty of Science and Technology

Molecular packing

Well known…

Hydrogen-bonding
Halogen-bonding

"Emerging"

Secondary-bonding
M···M interactions
M···H interactions
Interactions involving chelate rings

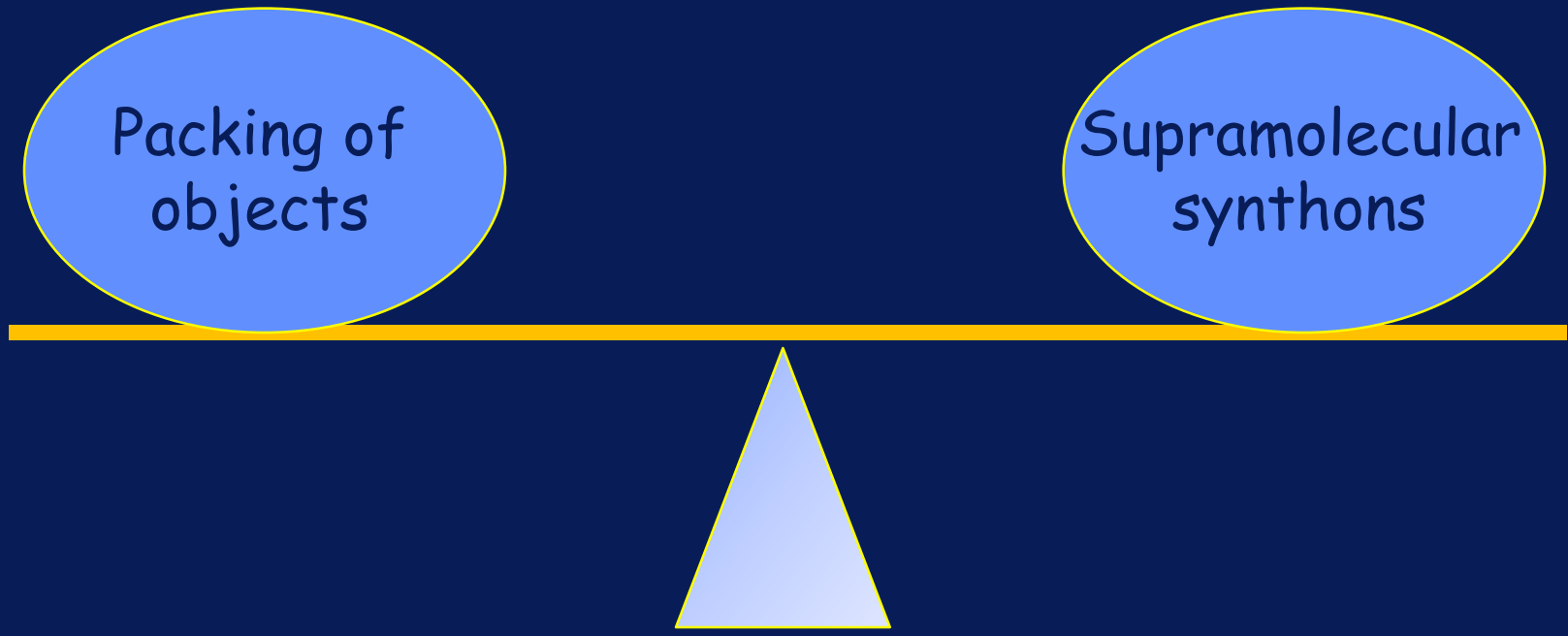
Caveat

Supramolecular synthon approach

versus

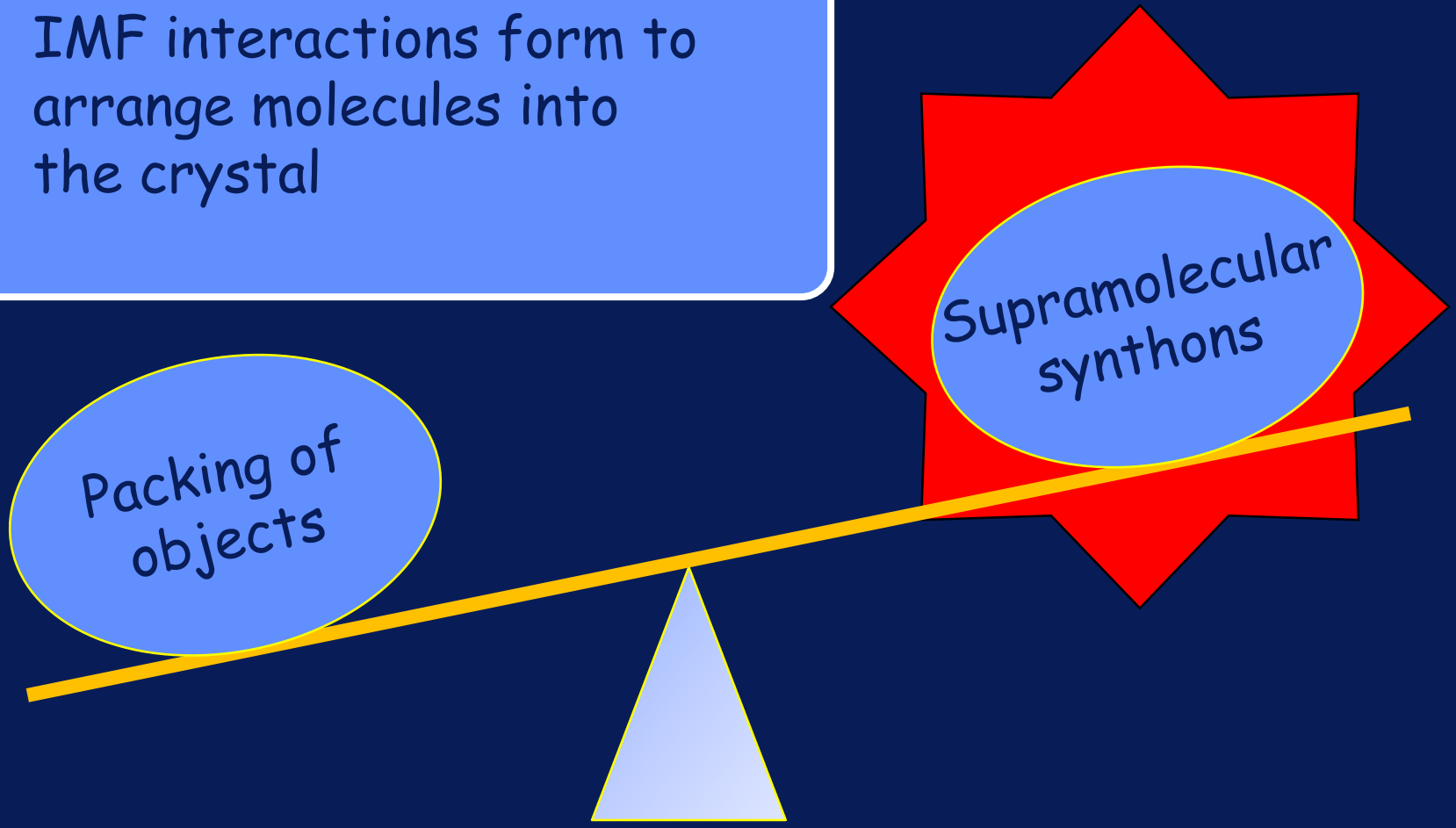
Global crystal packing approach

Factors that Control Molecular Packing

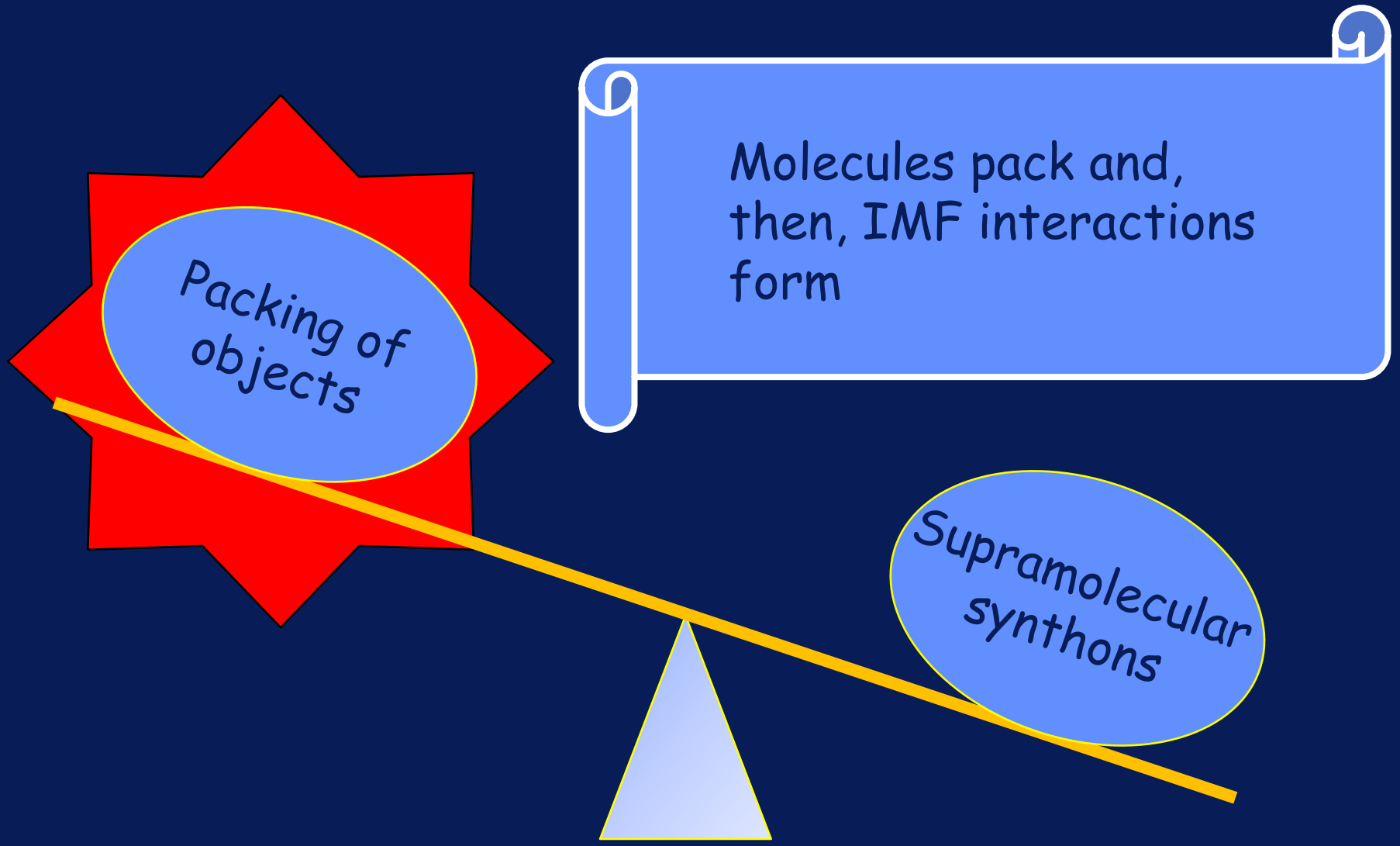


Factors that Control Molecular Packing

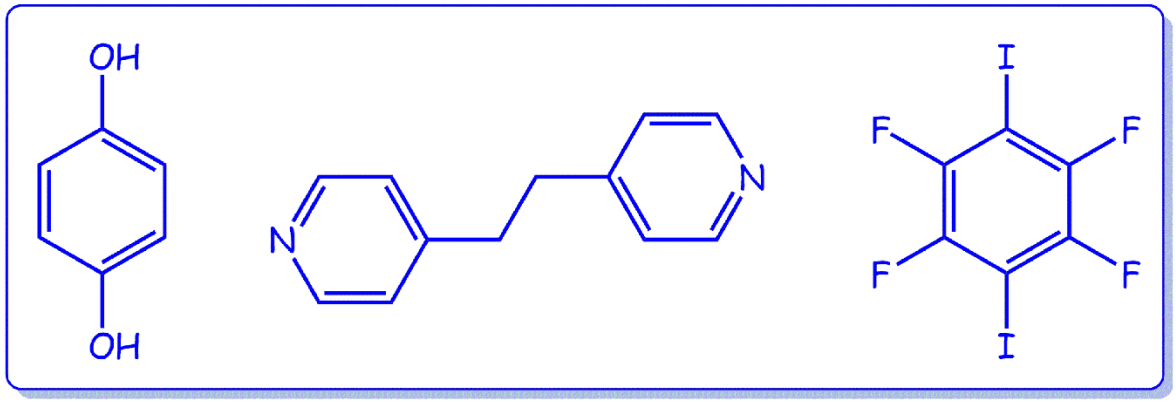
IMF interactions form to arrange molecules into the crystal



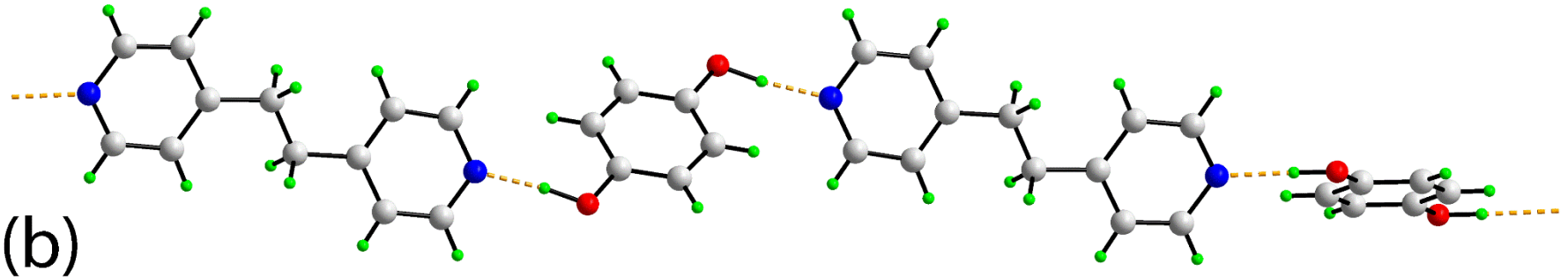
Factors that Control Molecular Packing



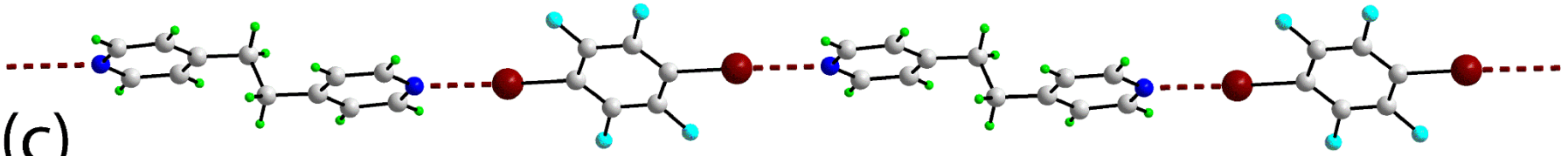
Hydrogen-Bonding versus Halogen-Bonding



(a)

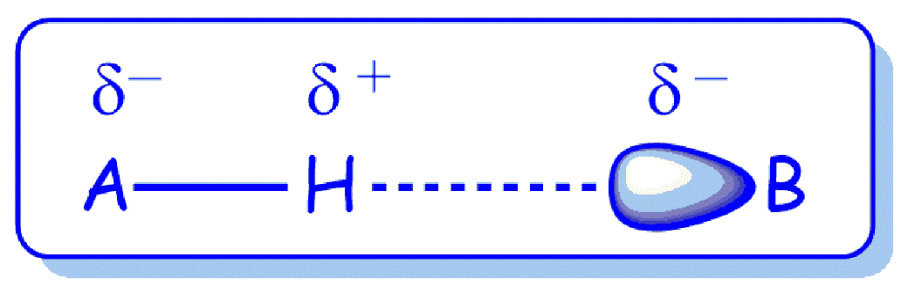


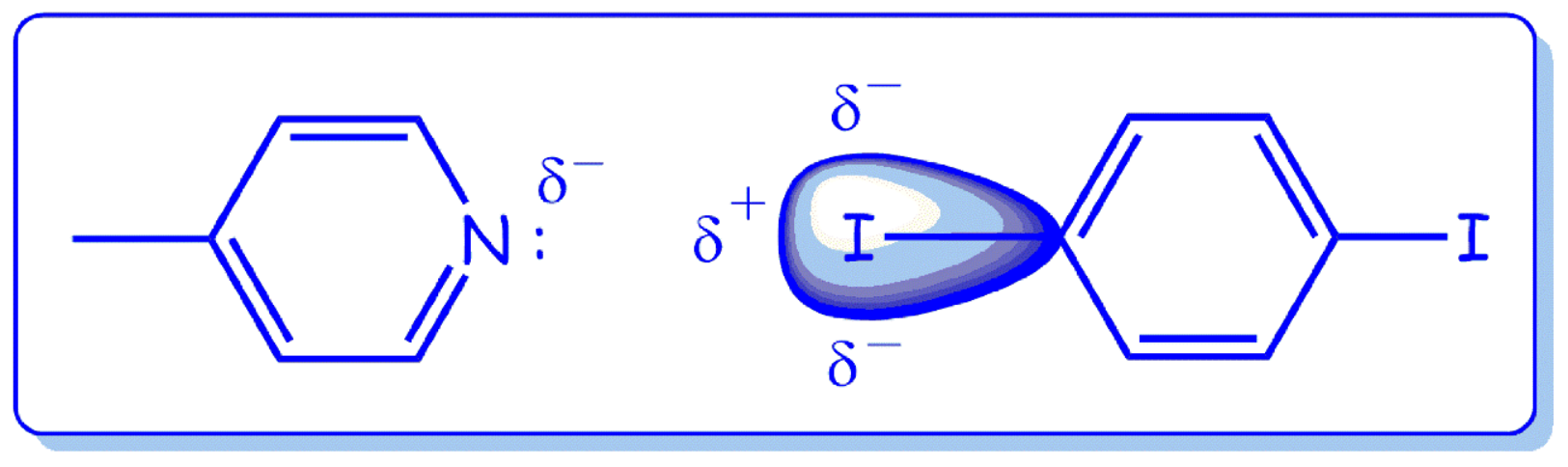
(b)



(c)

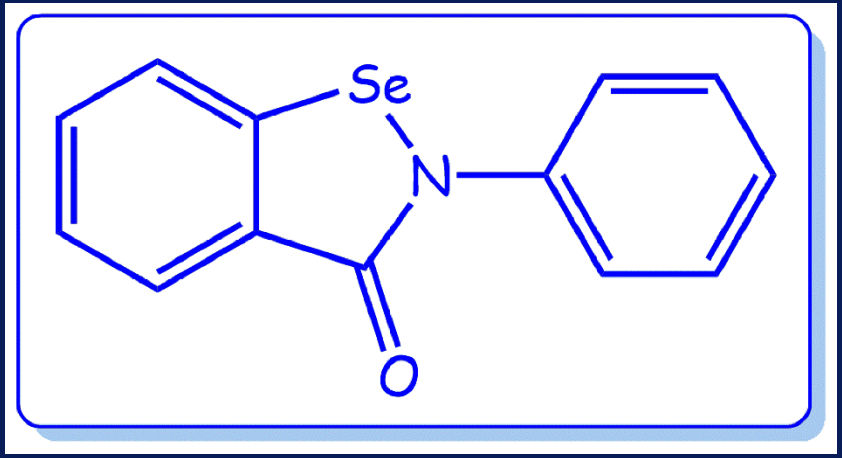
Hydrogen-Bonding vs Halogen-Bonding



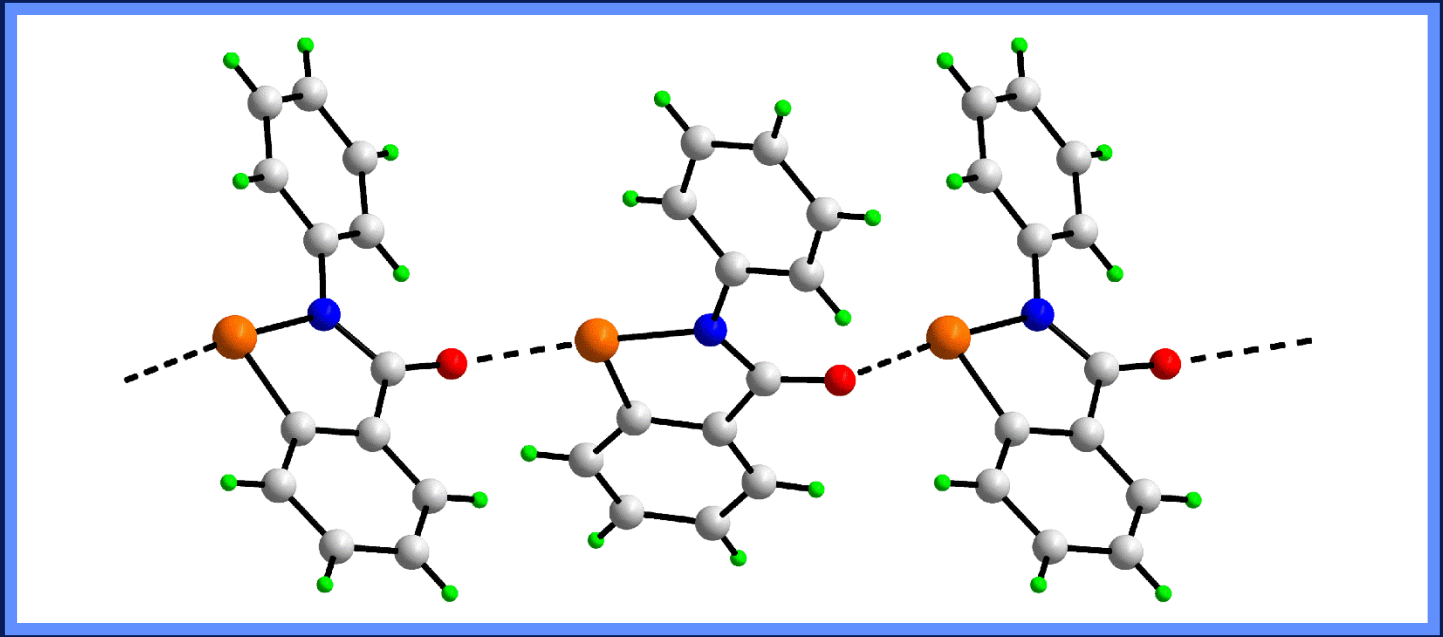


polar gap, σ-hole

Tetrel, Pnictogen and Chaclogen Secondary-Bonding

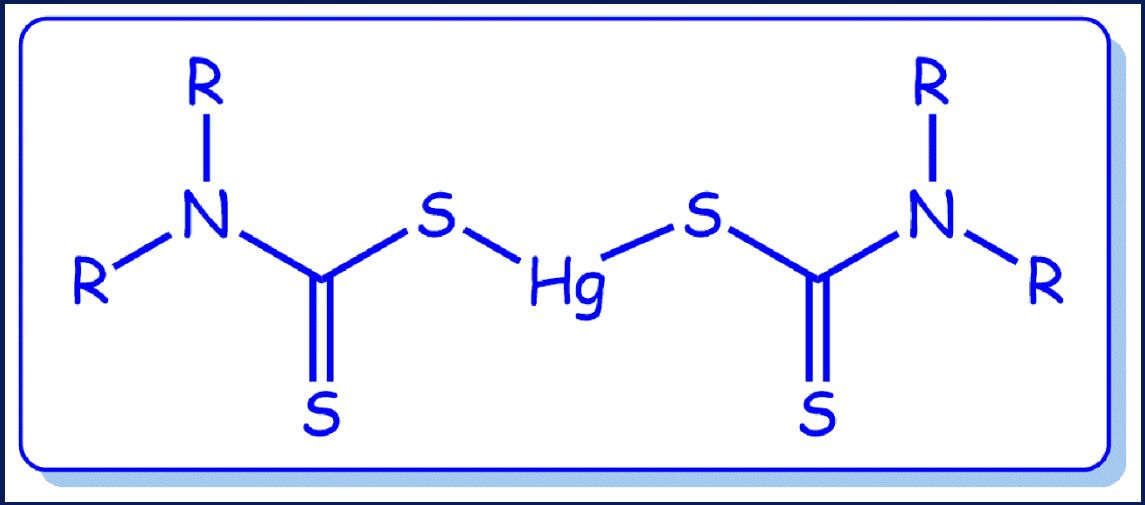


Tetrel, Pnictogen and Chaclogen Secondary-Bonding



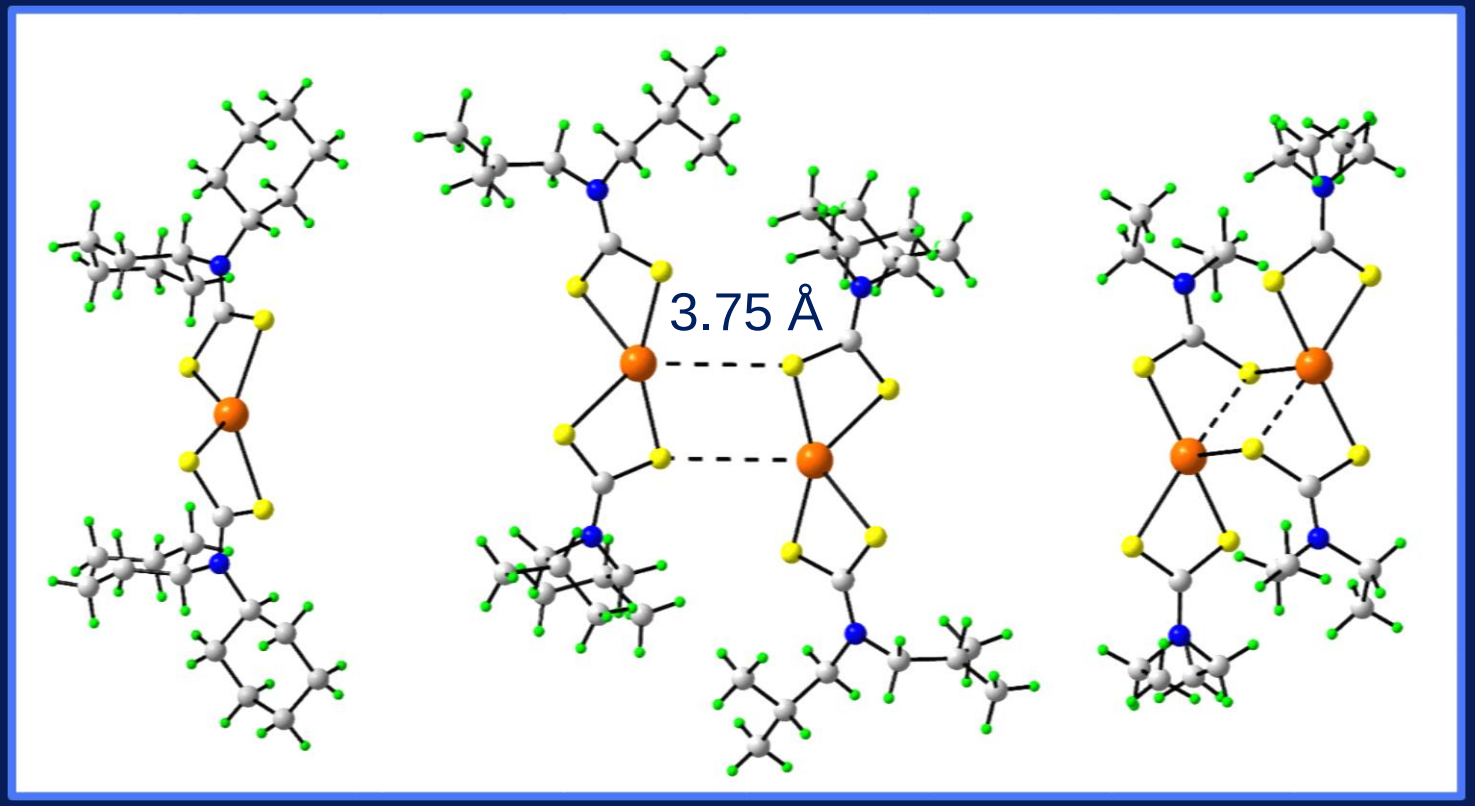
Se···O in Ebselen®
polar gap, σ-hole; ~8 kcal/mol

Steric effects and Secondary-Bonding



"$Hg(S_2CNR_2)_2$"

Steric effects and Secondary-Bonding

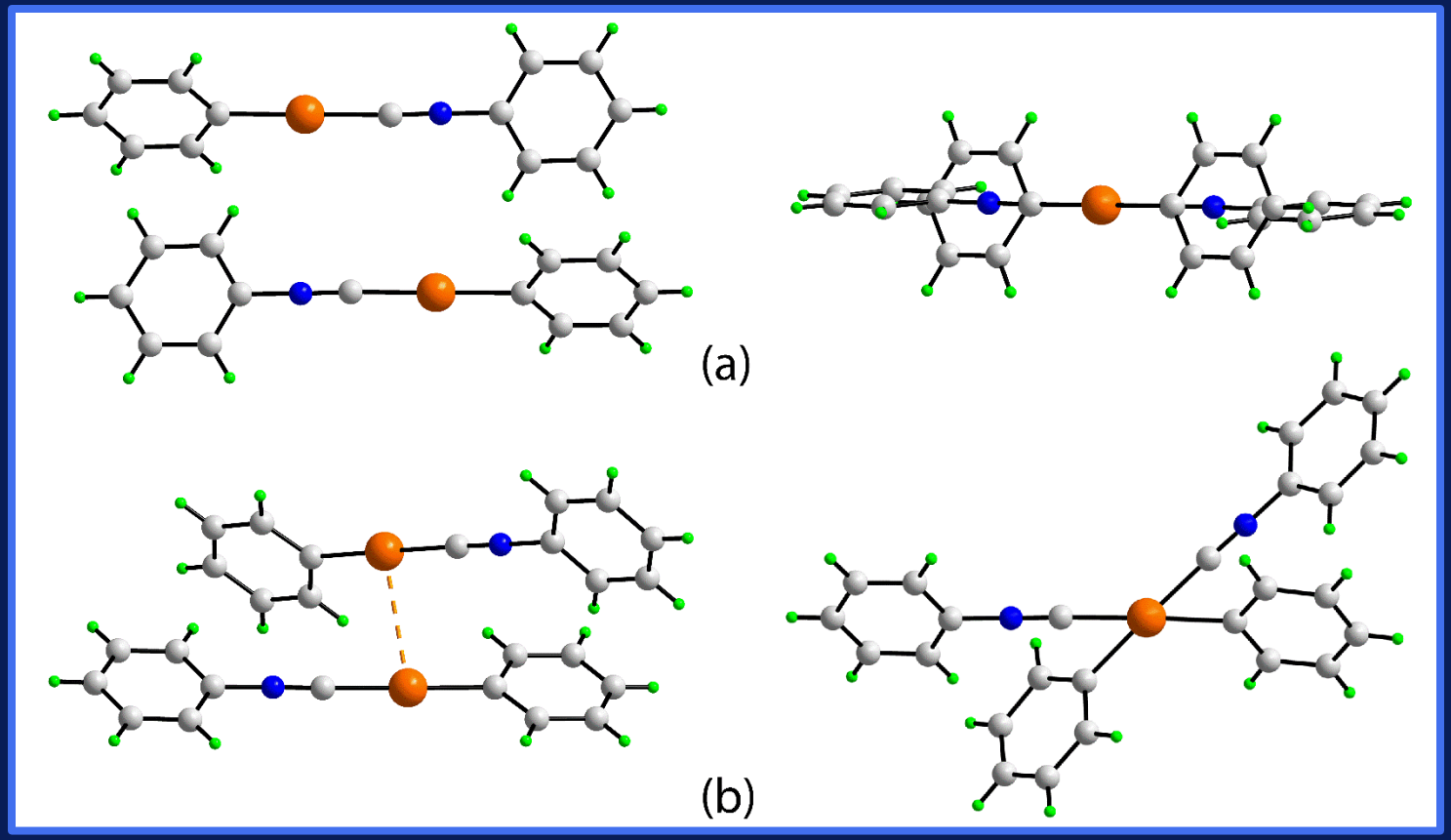


"$Hg(S_2CNR_2)_2$"

Sum of the van der Waals radii for Hg and S = 3.35 Å

← increasing size of R

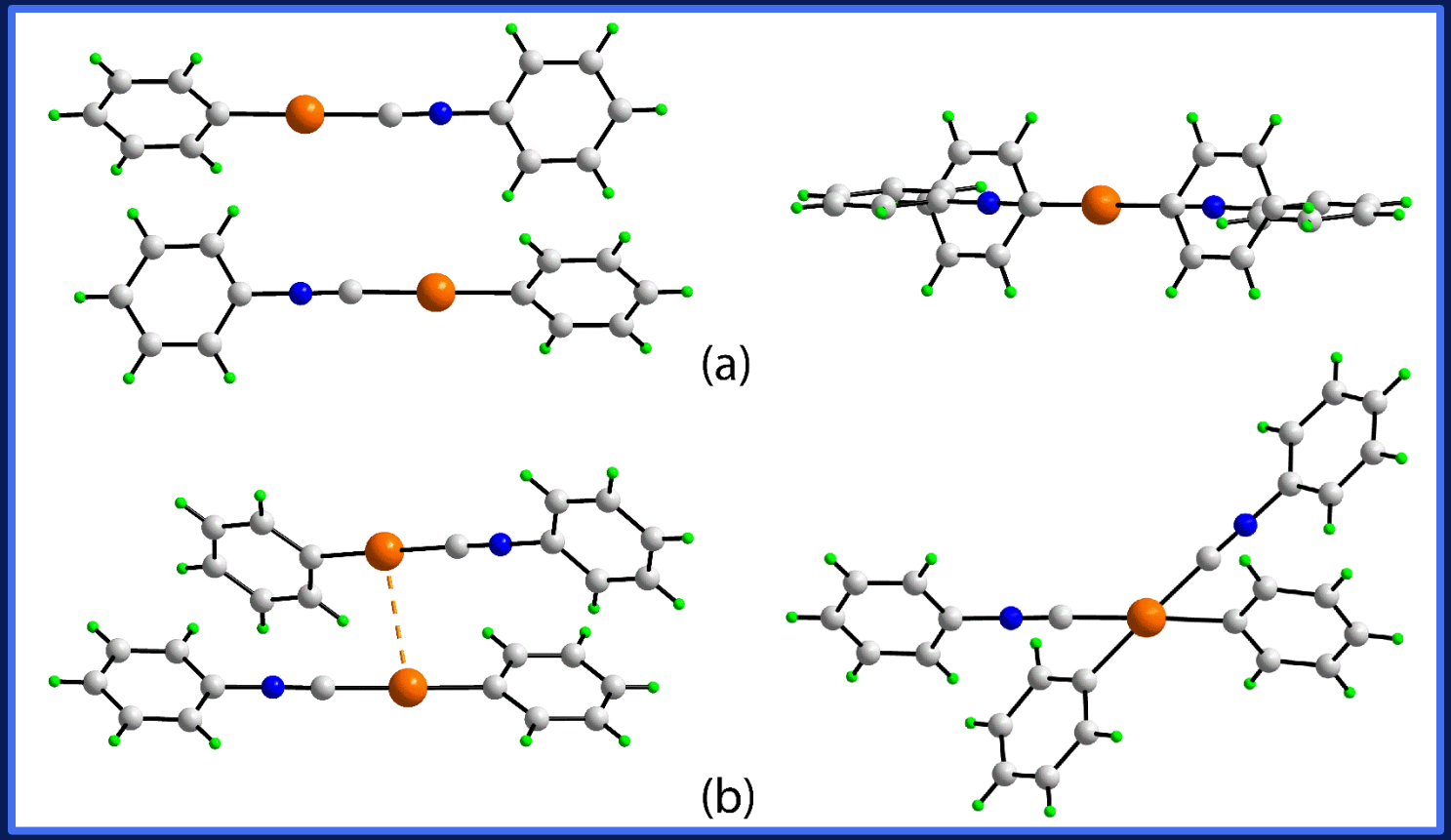
Aurophilic (Au···Au) interactions



Polymorphs of PhAuC≡NPh
(a) to (b) Touch of a needle / mechanical grinding

Ito *et al.*, 2013

Aurophilic (Au···Au) interactions

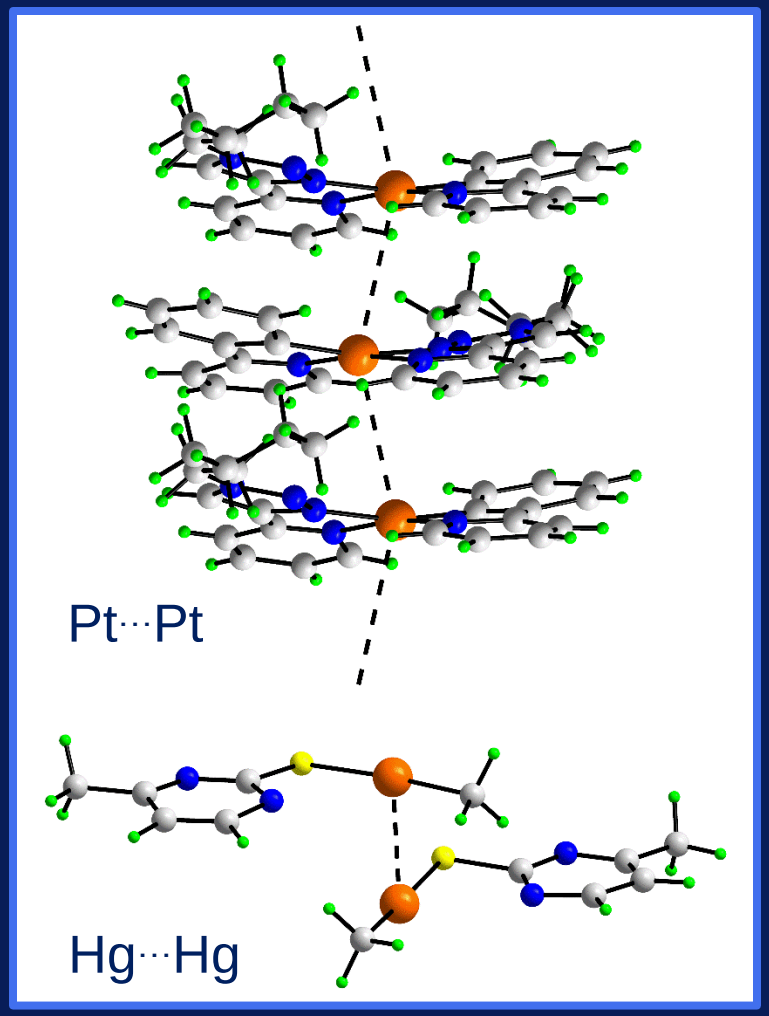


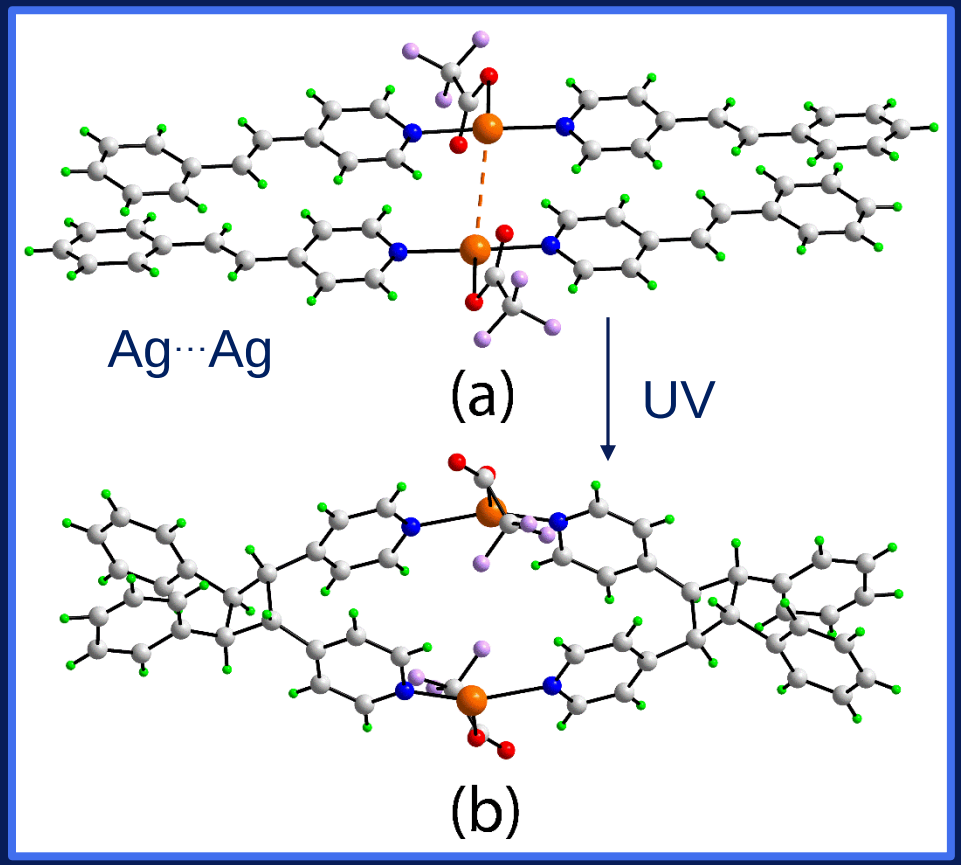
Polymorphs of PhAuC≡NPh
(a) to (b) Touch of a needle / mechanical grinding

6-12 kcal/mol

Ito *et al.*, 2013

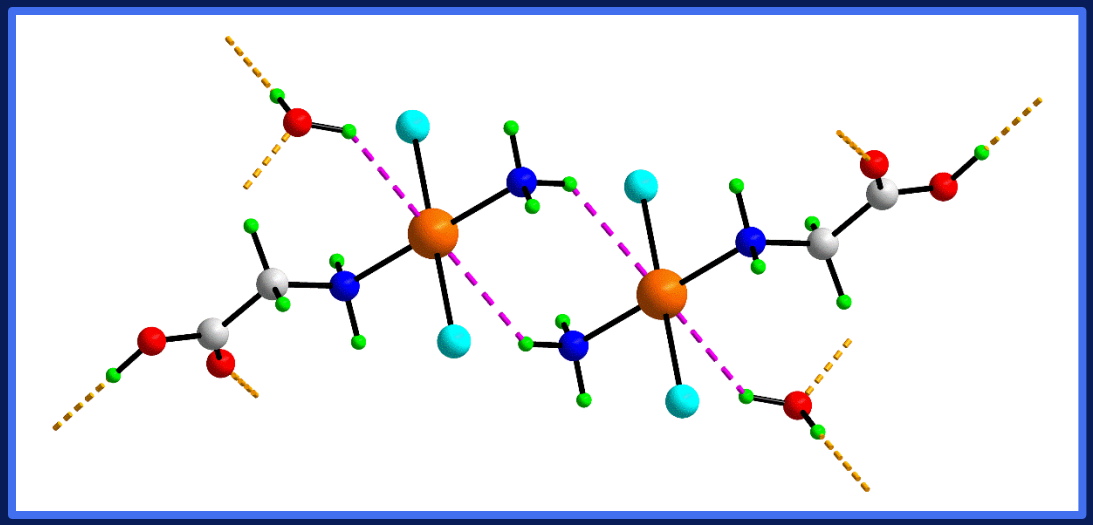
Heterometallophilic (M···M') interactions





Krikorian *et al*., 2014; Bravo *et al*., 1986; Chu *et al*., 2005

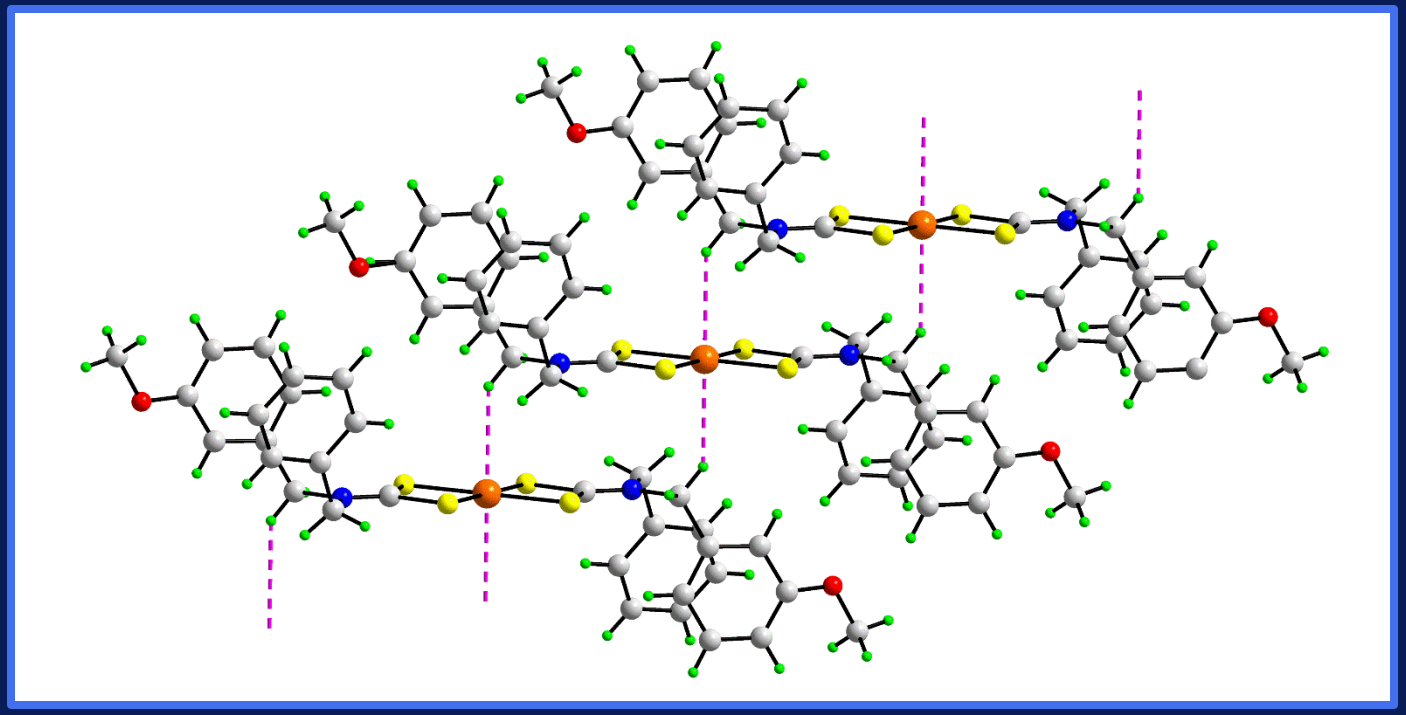
Metal···hydrogen interactions as supramolecular synthons



Pt···H-N and Pt···H-O hydrogen bonding in trans-[$PtCl_2(NH_3)$(N-glycine)]

Rizzato *et al.*, 2010

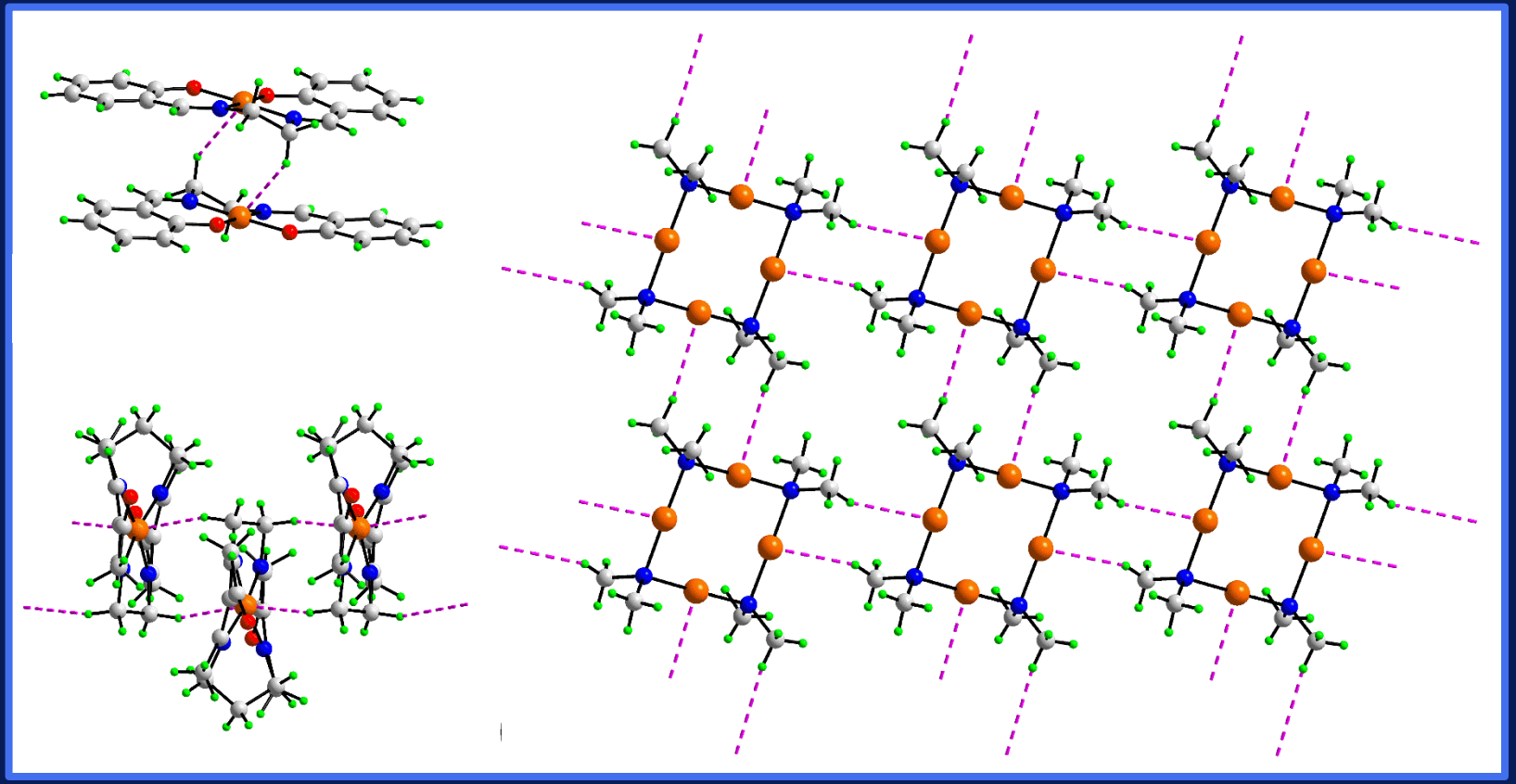
Metal···hydrogen interactions as supramolecular synthons



Ni···H interactions in $Ni(S_2CNRR')_2$

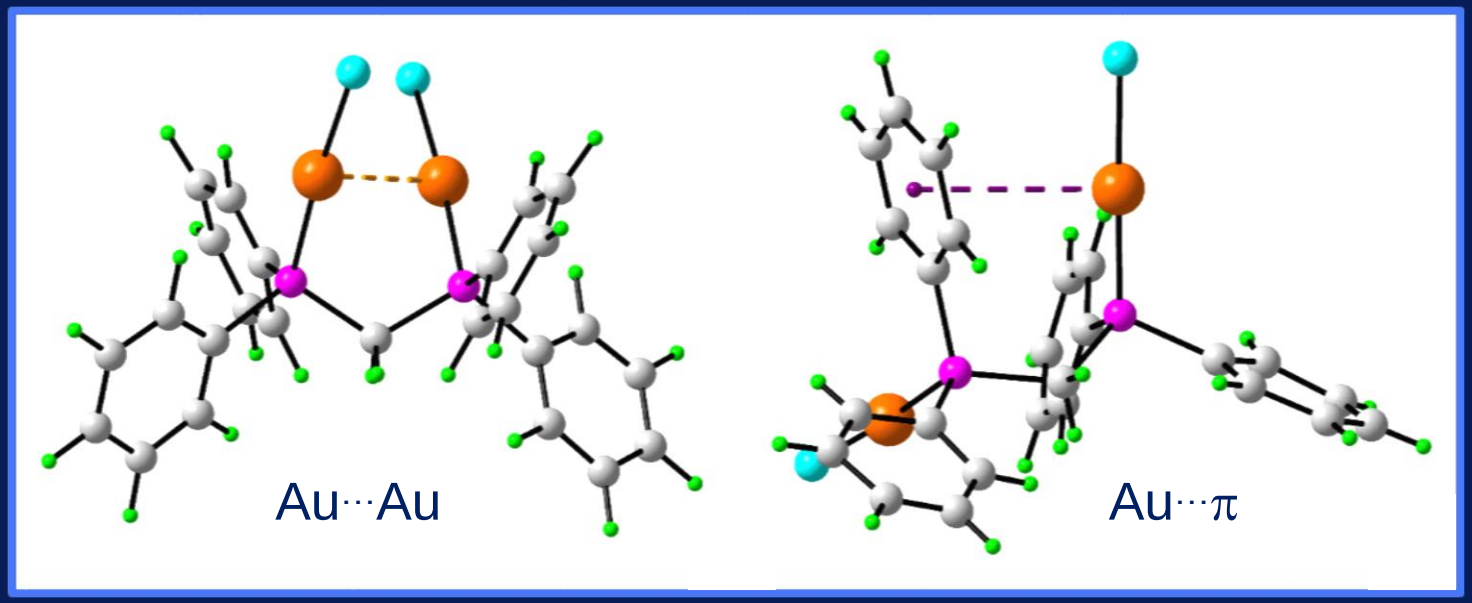
Singh *et al*., 2013

Metal···hydrogen interactions as supramolecular synthons



Architectures sustained by $\{\cdots HCNM\}_2$ synthons
cf. $\{\cdots HOC{=}O\}_2$

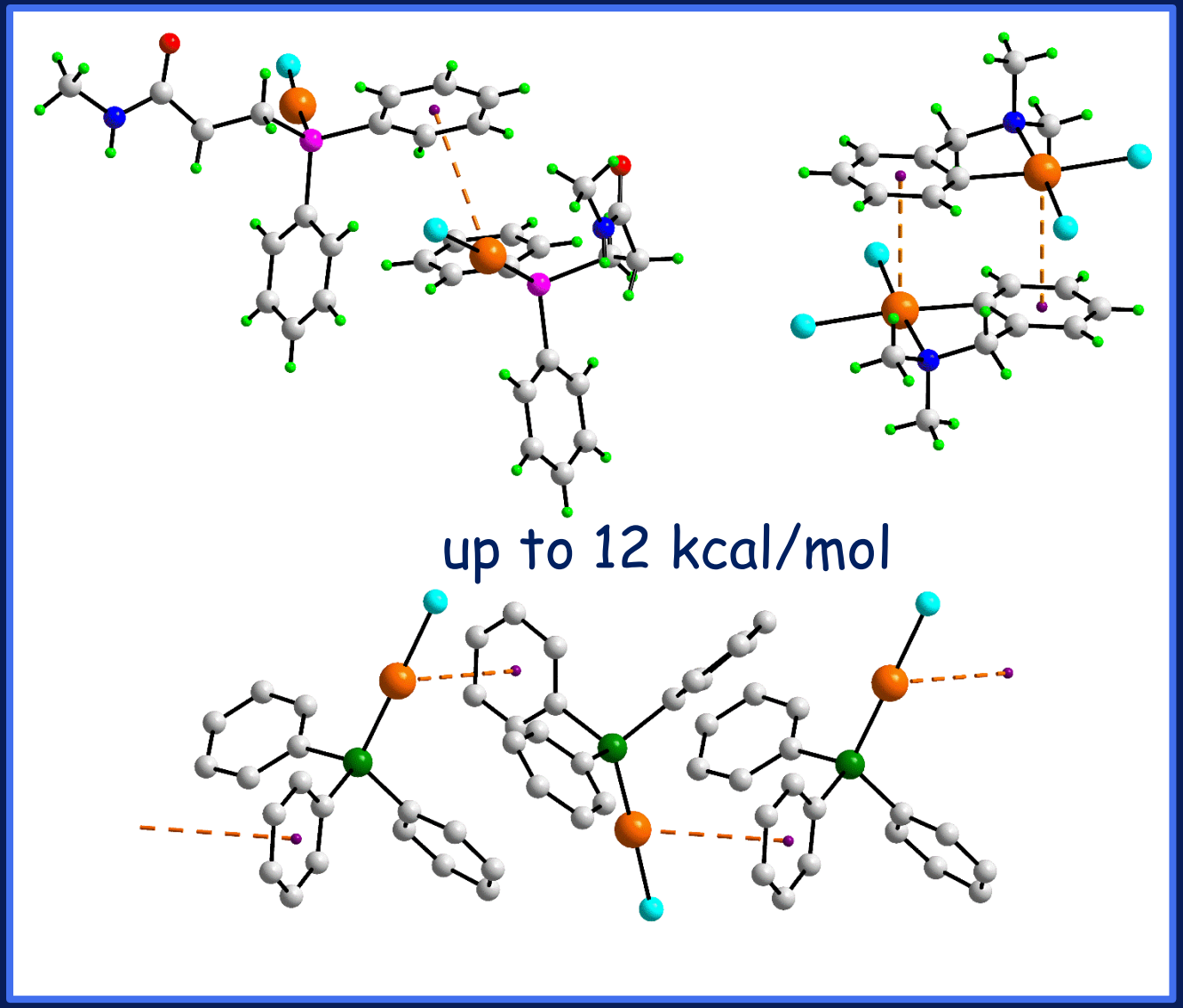
Au···π(arene) interactions



Polymorphs of $(Ph_2PCH_2PPh_2)(AuCl)_2$

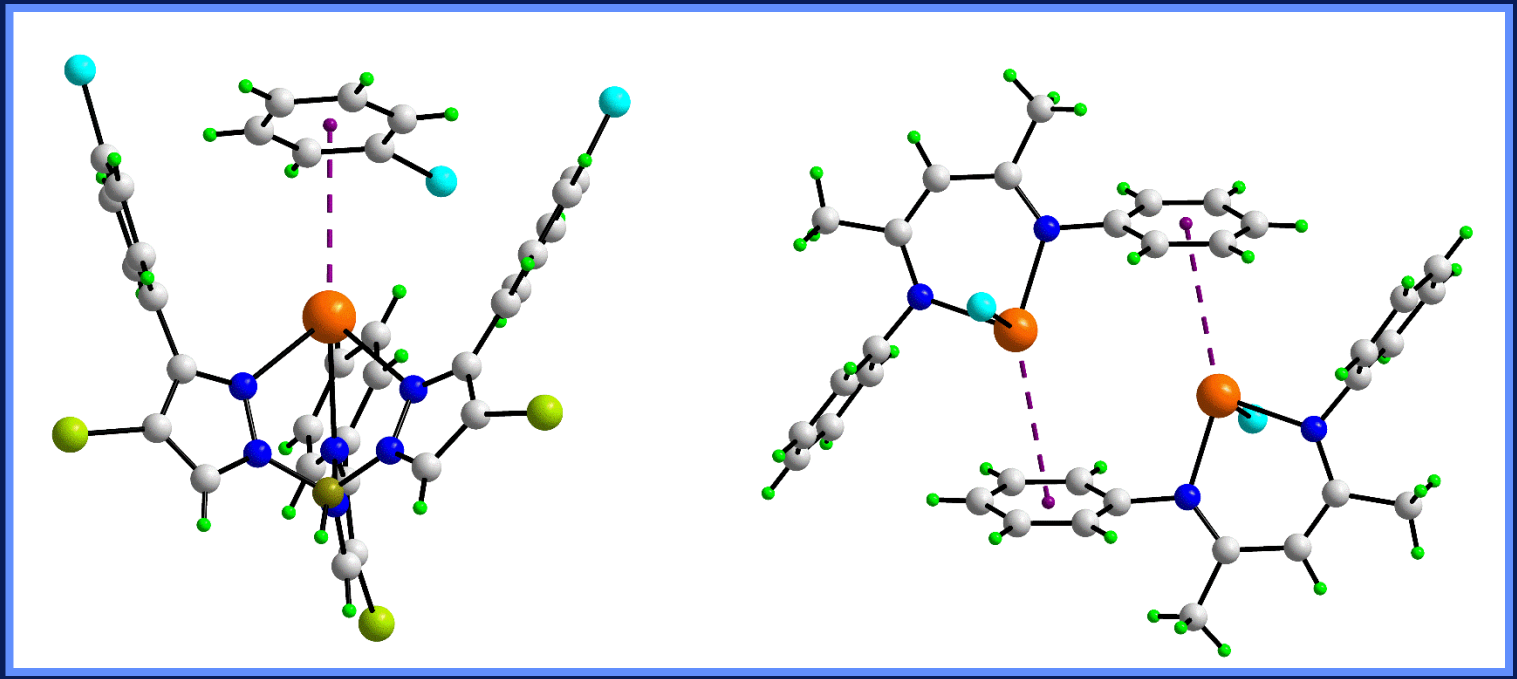
Intermolecular Au···π(arene) interactions

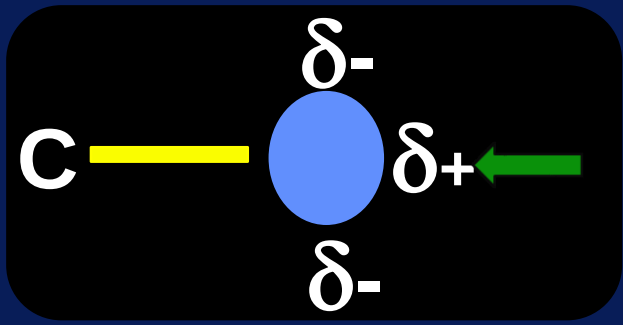
0-D



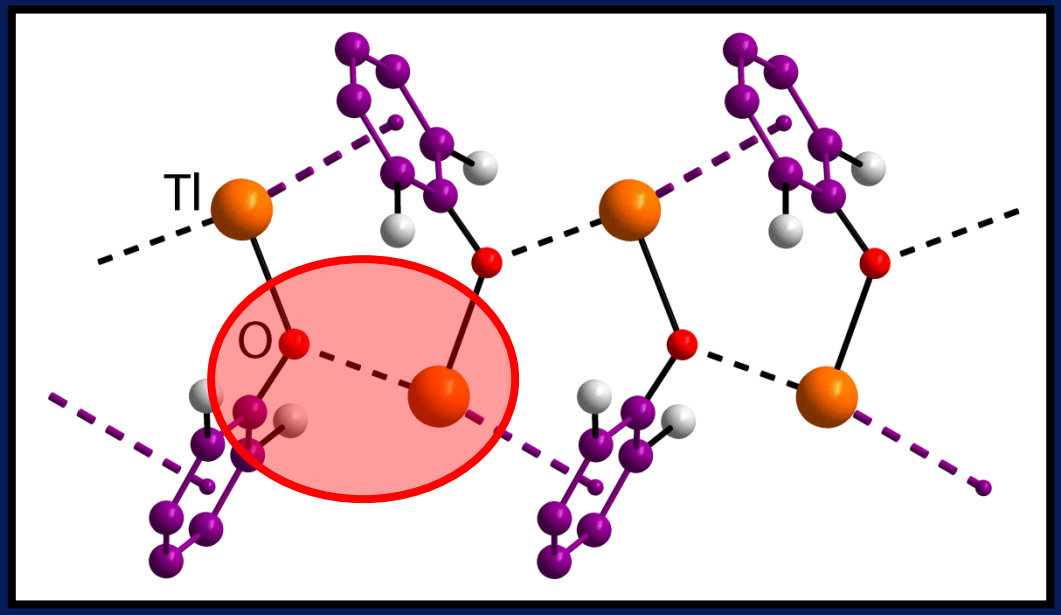
1-D

Intermolecular M(lp)···π(arene) interactions





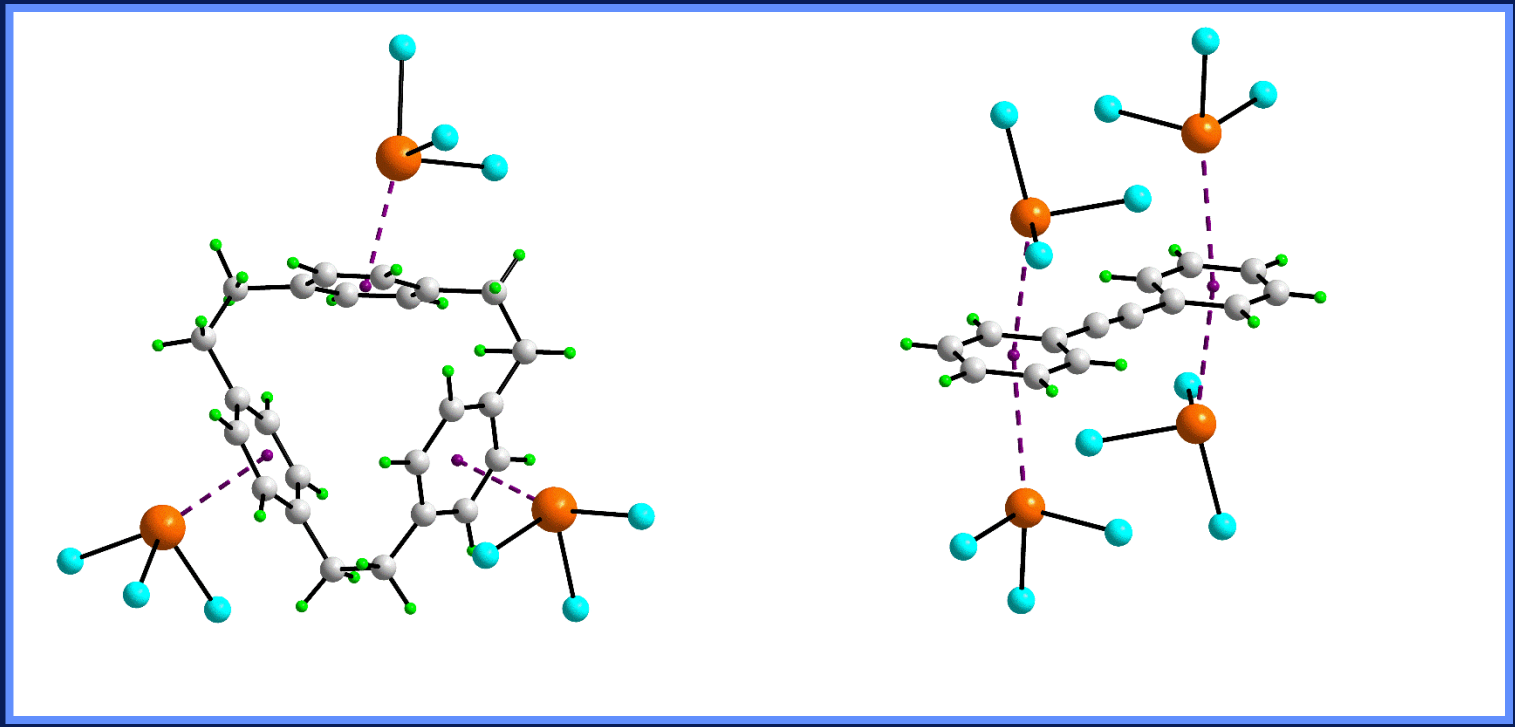
Tl(lone pair)…π(arene) Interactions



d = 3.16 Å, α = 4.2°

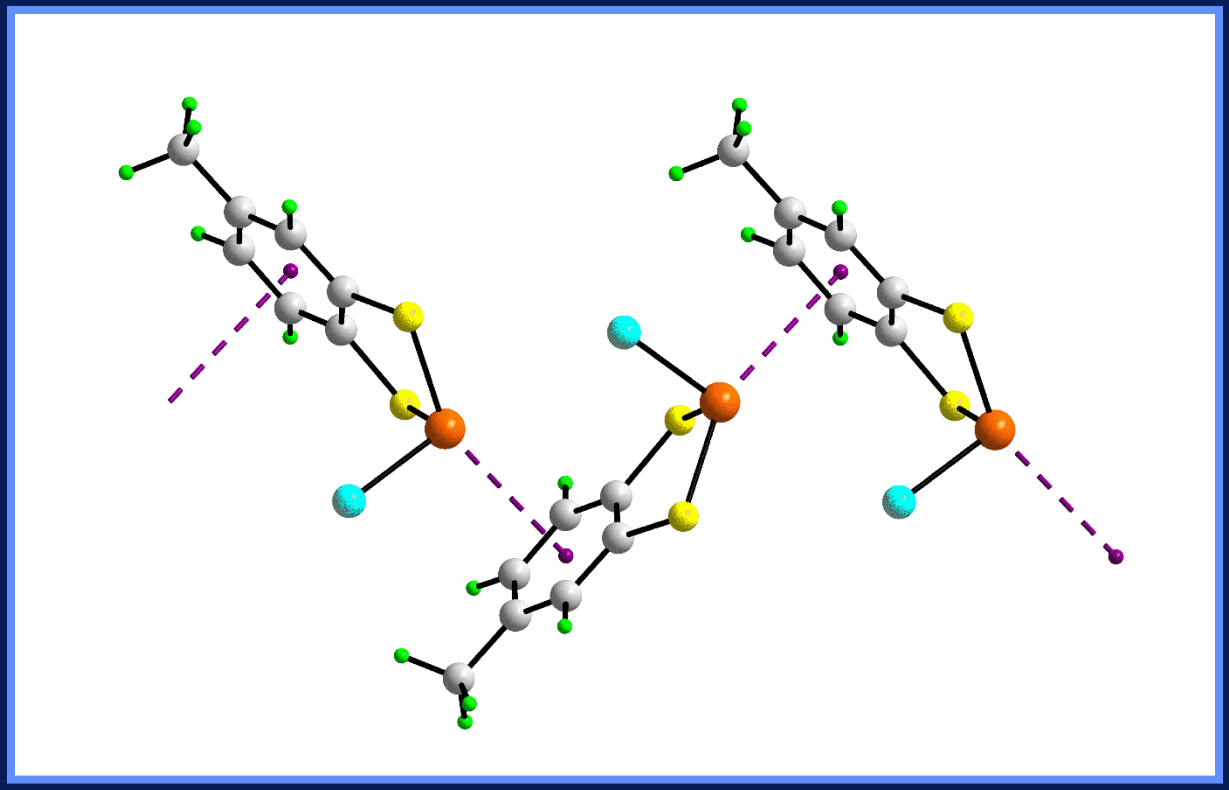
Excluded, as Tl(lp)…π not operating in isolation

Intermolecular M(lp)···π(arene) interactions

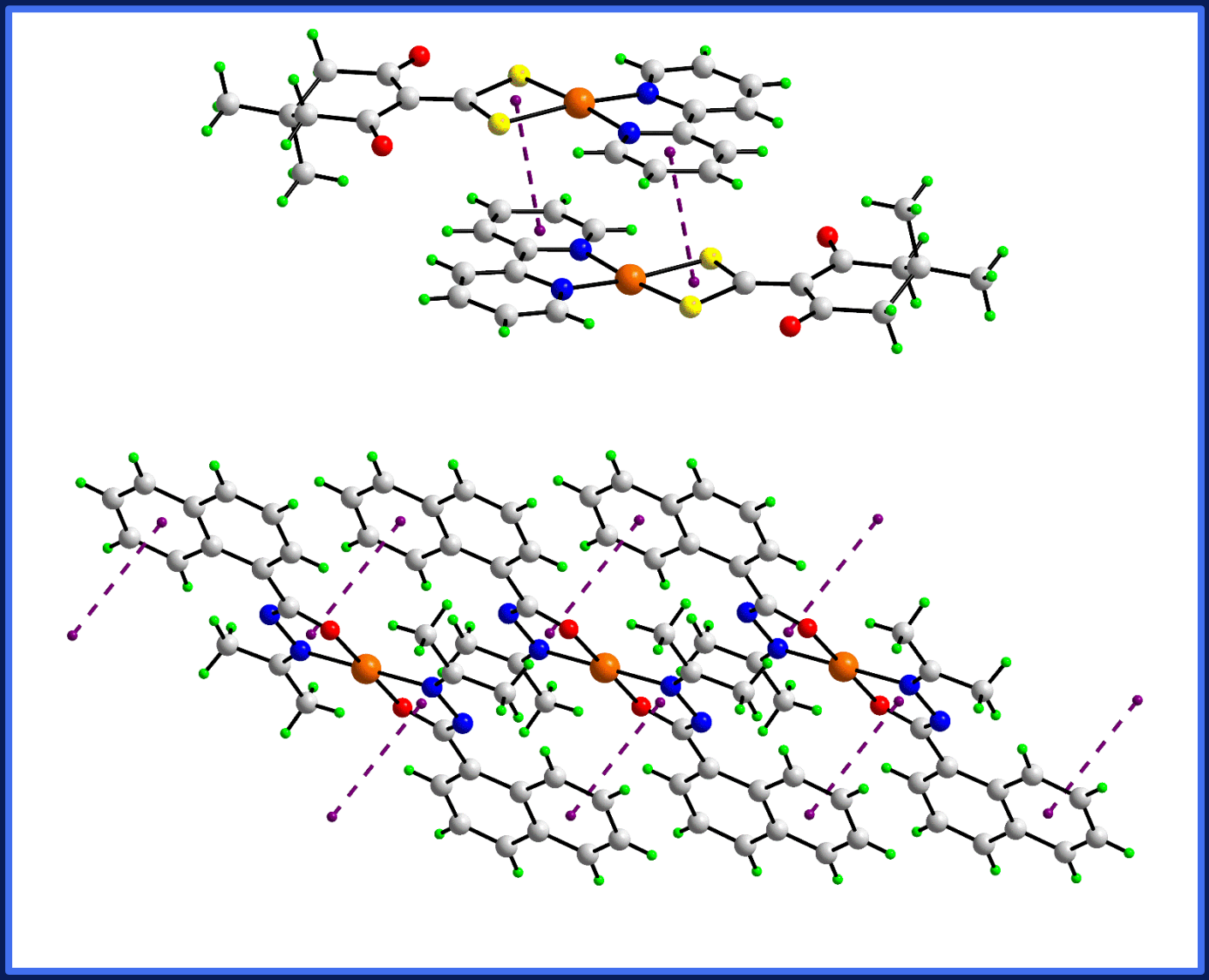


up to 10 kcal/mol

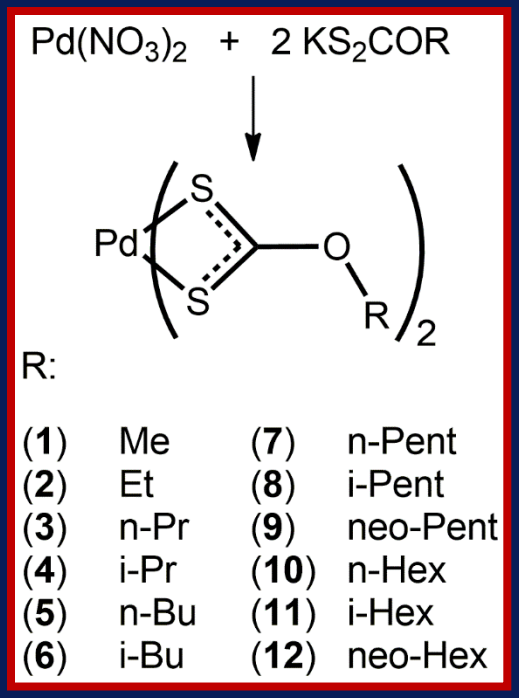
Intermolecular M(lp)···π(arene) interactions

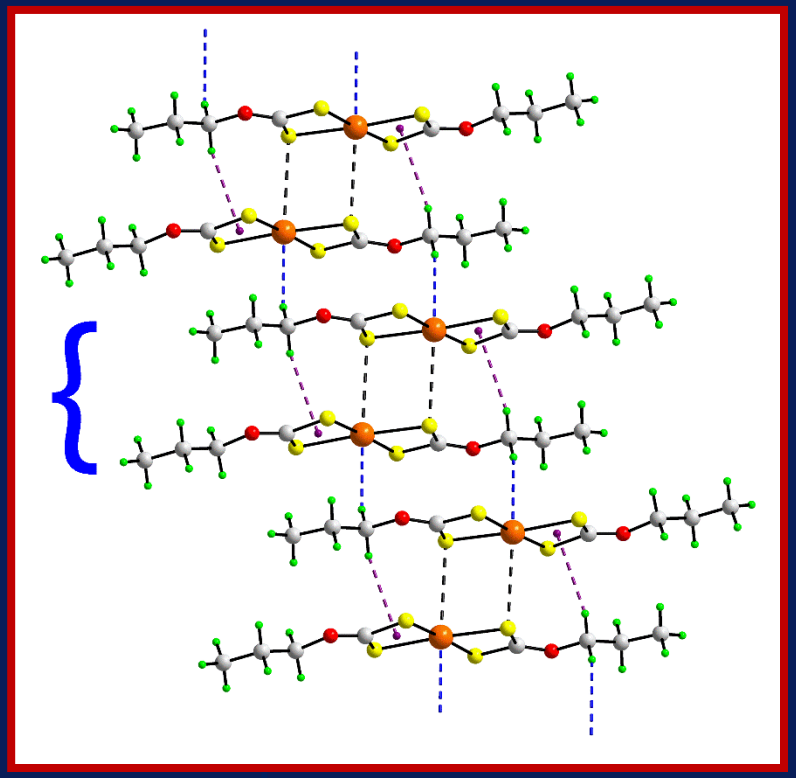


Intermolecular interactions involving chelate rings

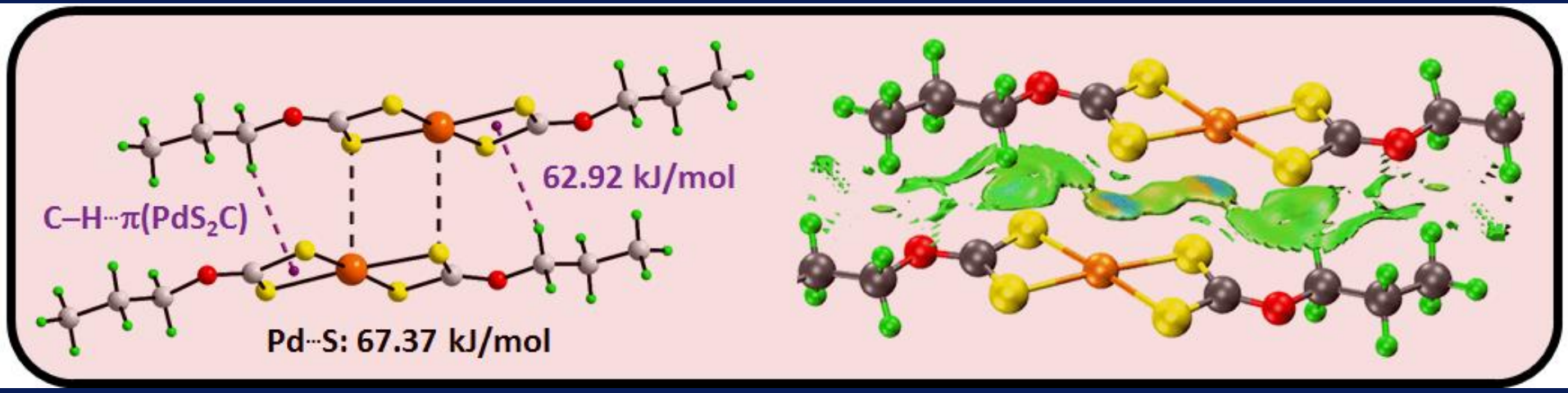


Intermolecular interactions involving chelate rings



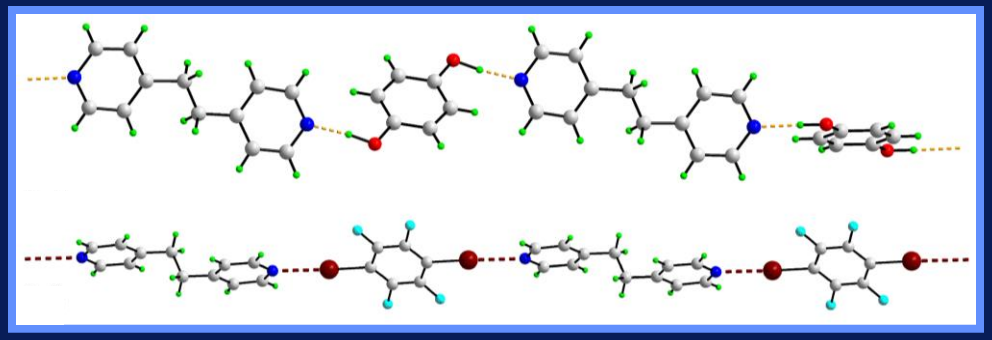


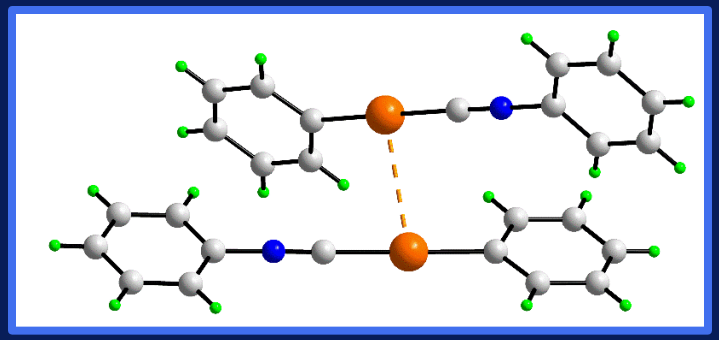
Intermolecular interactions involving chelate rings



up to 4 kcal/mol

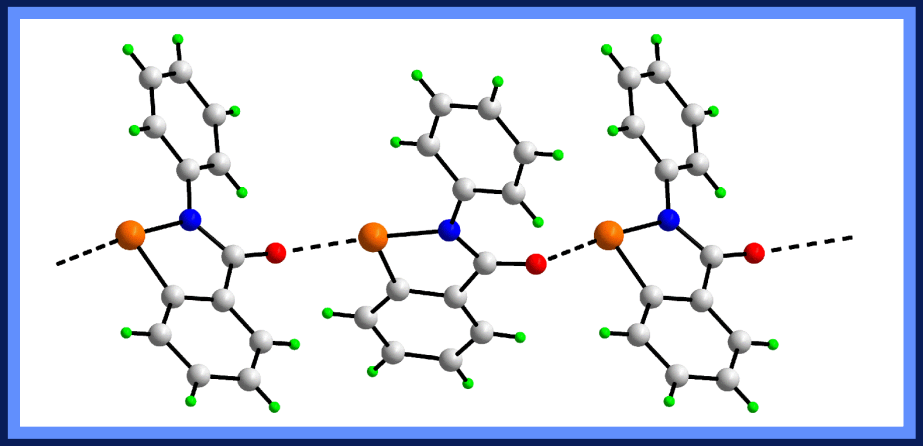
Overview



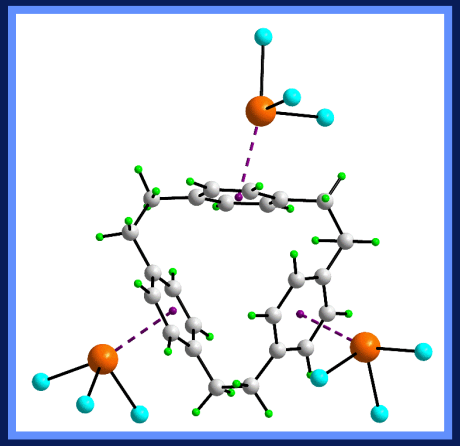


6-12 kcal/mol

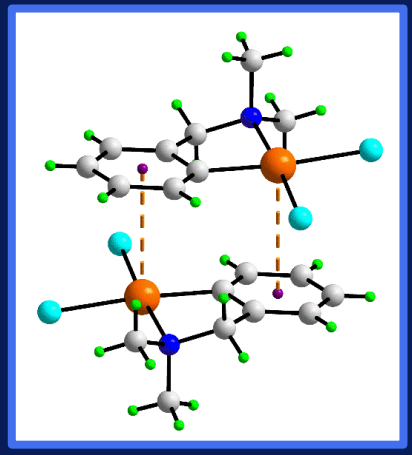
8 kcal/mol



10 kcal/mol



12 kcal/mol



Conclusions

More than hydrogen bonding

Energies of “emerging” interactions similar

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Fortuna Eruditis Favet ("*Fortune favours the prepared mind*")

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